Consumer and Corporate Affairs Canada | Consommation et Corporations Canada

(11) (A) No. 1 257 745

(45) ISSUED 890718

(52) CLASS 402-624
C.R. CL. 18-978;
204-91.74

(51) INT. CL. B29C 61/00,
B29K 23/00, C08L 23/06
4

(19) (CA) **CANADIAN PATENT** (12)

# (54) Recoverable Polyethylene Composition and Article

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(21) APPLICATION No. 474,753

(22) FILED 850220

(30) PRIORITY DATE (GB) U.K. (582105) 840221

No. OF CLAIMS 21

Canada

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CCA-274 (11-82)

4/4/83

## ABSTRACT

## RECOVERABLE POLYETHYLENE COMPOSITION AND ARTICLE

This invention discloses a recoverable composition an article comprising cross-linked polyethylene. The polyethylene has a molecular weight greater than about 3.0 million.

# DESCRIPTION

## RECOVERABLE POLYETHYLENE COMPOSITION AND ARTICLE

This invention relates to crosslinked polyethylene compositions and their use in heat-recoverable articles.

A wide range of polyethylenes is commercially available. As stated in ASTM D-4020-81, the term ultra-high-molecular-weight polyethylene (UHMW-PE) is used to denote linear polymers of ethylene which have a relative viscosity of 2.30 or greater, as per the test procedures described in the ASTM.

Certain of the polyethylenes may be imparted with shape memory. Crosslinking, either by chemical curing or by radiation, improves the shape memory of the polyethylenes. Work on very high molecular weight polyethylenes has been previously disclosed in British Patent Specification 1,095,772. In this reference, polyethylenes having a molecular weight in excess of 1 million were crosslinked and compared against non-crosslinked polyethylenes of similar molecular weight. Certain mechanical properties of both groups of polyethylenes were measured at temperatures above their respective melting points.

A true measure of the effectiveness of shape memory is the recovery force. Recovery force can be characterized by stress relaxation behavior as determined by a stress relaxation test. In this test, a sample is stretched at constant strain rate to a particular length and then with the strain rate set at zero, the stress as a function of time is measured.

It is desirable to have a recoverable material with a higher recovery force as a function of time than is currently recognized or available. The British reference failed to appreciate the value of recovery force and, further,

considered only very high molecular weight polyethylenes rather than ultra-high-molecular-weight polyethylenes.

Thus it is an object of this invention to have a recoverable polyethylene having a high recovery force.

It is another object of this invention to have a recoverable polyethylene having a high recovery force which is suitable for use as an engineering material.

A first aspect of the invention provides articles, in particular heat-recoverable articles, which are composed of a composition comprising crosslinked polyethylene obtained by crosslinking polyethylene which has a relative viscosity of 2.3 or more and a molecular weight greater than about 3.0 million, as defined by ASTM D-4020-81. The crosslinking of the polyethylene may be accomplished by any of the known methods such as by radiation or by chemical curing. The preferred crosslinking method is by radiation.

A second aspect of the present invention provides a process for the preparation of a heat-recoverable article, which process comprises

(1) crosslinking an article composed of a composition comprising polyethylene which has a relative viscosity of 2.3 or more and a molecular weight greater than about 3.0 million, as defined by ASTM D-4020-81; and

(2) expanding the crosslinked article from step (1) at a temperature below the melting point of the composition, thus rendering it heat-recoverable.

Embodiments of the present invention will now be described, by way of example, with reference to the accompanying drawings, wherein:

Figure 1 illustrates stress relaxation curves for the polyethylene of the present invention in the unbeamed (non-irradiated) condition;

Figure 2 illustrates stress relaxation curves for the polyethylene of the present invention in the beamed condition;

Figure 3 illustrates the stress relaxation curves of Figure 2 on a larger time scale; and

Figure 4 is similar to figure 2 but illustrates another aspect of the invention.

Referring to the drawings, Figure 1 illustrates stress relaxation curves for various polyethylenes ranging in molecular weight from .6 million to 5.0 million. Polyethylene tensile specimens in the unbeamed state were cut out of a UHMWPE sheet. The tensile specimens were subjected to tensile tests on an Instron (a trademark) with the crosshead speed set at 12.7 cm (5 inches) per minute. When the crossheads moved from a separation distance of 3.0 cm (1.2 inches) to 10.7 cm (4.2 inches), so that a 2.5 cm (1 inch) length on the tensile speciman became 8.9 cm (3.5 inches), the strain rate of the Instron was set at zero. Then the stress as a function of time was measured and plotted. The tests were conducted at a temperature of 120° C. As illustrated in the figure, most of the specimens are grouped together in the same range, the exception being the .6 million molecular weight specimen which stands off by itself. Similar specimens were prepared but were subjected to irradiation so as to become crosslinked. The results of the testing of these specimens are shown in Figs. 2 and 3. Once the specimens have been beamed, it is clear that the polyethy-lenes can now be grouped into two distinct categories: those

polyethylenes less than about 1.5 million in molecular weight and those polyethylenes greater than about 3.0 million in molecular weight. This large disparity between the two groups of polyethylenes was totally surprising and unexpected. Further, the gap cannot be accounted for solely by the differences in molecular weight of the material.

Stress relaxation is an important parameter for these polyethylenes because it is directly indicative of the recovery force of this material. The higher the stress at any given time, then the higher the recovery force. The higher recovery force of this material makes it suitable for uses which were heretofore unknown in the prior art.

The preferable recovery force may be defined more particularly with reference to Figure 4. Figure 4 is similar to Figure 2 except that Figure 4 now includes two straight lines A and B. Lines A and B approximate the preferred ranges of the recovery force over the times of 0.1 to 30 minutes and at a temperature of 120°C.

Line A may be defined by the equation:

$$\text{Recovery Force} = 1750 - 275.\log(t)$$

where the recovery force is the stress (psi) at any unit of time and t is the time in minutes. Line A actually describes the lower limit of one preferred range of recovery force. Thus it is preferred that at any unit of time and at 120°C., the recovery force should be above line A.

Line B may be defined by the equation:

$$\text{Recovery Force} = 2474 - 275.\log(t)$$

where, again, the recovery force is the stress (psi) at any unit of time and t is the time in minutes. Line B, however, describes the more preferred range of recovery force. It is most preferred that at any unit of time and at 120o C., the recovery force should be above line B.

It is also preferred that the composition and articles of these inventions be recovered by an external heat source. The heat source may either be in the form of an intense source such as a torch or in a more general form such as oven heating. In any case, an evenly distributed heat flux which does not over heat the surface is needed in order to assure a high quality product.

It is preferable that the heat-recoverable composition be expanded at or below the melting point of the composition. More preferably, the composition should be expanded within the temperature range of room temperature to about 140°C. The melting point of these polyethylenes is actually a melting range which extends from about 130°C-140°C. 140°C is considered to be the upper end of the temperature range at which the material will be at least partially crystalline. Even more preferably, the composition should be expanded within a temperature range of room temperature to 125°C.

It has been found that the lower the temperature at which expansion occurs, the higher will be the recovery force. The lower end of the temperature range at which expansion can occur will be limited only by the force available to expand the composition. It can be appreciated that the lower the expansion temperature, the stronger will be the forces resisting expansion. When the material is expanded part of these forces resisting

expansion become the driving force for recovery. At the same time, stress relaxation tends to deplete this driving force. However, since stress relaxation decreases with decreasing temperature, the effect of stress relaxation will likewise decrease with decreasing temperature. Thus, since at lower temperatures stress relaxation is at a minimum, the net driving force, i.e., the recovery force, will approach a maximum at low temperatures.

It is preferable that the composition be recovered within the temperature range of room temperature to 140°C. More preferably, the composition should be recovered within the temperature range of 75°C to 120°C.

The objects of the invention can best be achieved when the following precepts are followed:

The composition is preferably recovered at a temperature such that the temperature at recovery is always greater than the temperature at expansion. Also the temperature at recovery is preferably at or less than the melting point of the material When these precepts are adhered to, it is found that the recovery force is at a maximum.

It can thus be seen that the instant invention diverges completely from the teaching of the aforementioned British reference where the temperatures of expansion and recovery were above the melting point of the material and the tempera-ture of expansion is greater than the temperature of recovery.

Embodiments of the present invention will now be described, by way of example, with reference to the following examples.

Example 1

The composition of the present invention was prepared in the following manner:

The resin Hostalen GUR 413, the ultra-high-molecular-weight polyethylene powder, was blended with antioxidants in a high-speed dry blender for about ten minutes. This compound was then loaded into a cylindrical sleeve mold. The compound was compacted in the mold in order to reduce its porosity. The Compaction pressure was 100kgf/cm$^2$ at room temperature for about five minutes. The compacted product was sintered under ambient air at 220°C. for thirty minutes. The applied pressure during sintering was 50kgf/cm$^2$.

Subsequent to sintering, the product was cooled in the mold under pressure at 300 kgf/cm$^2$to about 50°C., at which temperature the mold was opened and the product released. The size of the cylindrical sleeve was two inches in length with a 0.7 inch inside diameter and a 1.4 inch outside diameter.

The product was crosslinked by exposing it to a high-energy electron beam. Dosage was in the order of 6 megarads.

The cylindrical sleeve was then expanded at 80°C by a conical mandrel. After expansion, the inside diameter of the cylindrical sleeve was 6.35 cm (2.5 inches). The expansion ratio was 3.57X. The expansion ratio is the ratio of the inside diameter after expansion to the inside diameter before expansion. Subsequent to the expansion, the cylindrical sleeve was stored until ready for use.

Two pipes having 3.8 cm (1.5 inch) outside diameter were then inserted in either end of the cylindrical

sleeve so that the cylindrical sleeve would form a coupling. The whole assembly was inserted in an oven and shrunk at 120°C. Of course, after shrinking, the inside diameter of the cylindrical sleeve was 3.8"cm (1.5 inch) the same as the outside diameter of the pipes.

The recovery of the polyethylene around the pipes was so secure that the pipes could not be twisted in relation to the coupling. A seal which was gas-tight at 827 KPa (120 psi) was achieved.

Example 2

A second cylindrical sleeve was made according to Example 1. In this case, however, after it had been expanded, the sleeve was sliced into several rings with each ring having a length of about 0.6 cm (one-quarter inch). These rings would now be used as shrink rings. In this case, a rubber sleeve was placed over an electrical connector and then the shrink ring was placed over the rubber sleeve and shrunk at 120°C in an oven. When the shrink ring was shrunk, it provided a water-tight seal so that water was prevented from entering between the rubber sleeve and the electrical connector.

Example 3

A third cylindrical sleeve was made according to Example 1. This sleeve was sliced into sections of about 2.54 cm (1 inch) in length. This 2.54 cm (1 inch) section was then recovered upon a substrate which would then be used as a bearing means. The bearing means would have a bearing surface. In this case, the outer periphery of the bearing means represents the bearing surface and the recovered polyethylene forms at least a portion of this bearing surface. It has been found

that this bearing means may be used as a rotatable article. Due to the high recovery force of the crosslinked polyethylene of this invention, there is no possibility of slippage between the recovered polyethylene and the substrate.

Recoverable articles employing the composition of this invention may be expanded up to about ten times its original inside diameter, although expansion up to eight times its original diameter is much preferred. Modifications may be made within the scope of the claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An article which is composed of a composition comprising crosslinked polyethylene obtained by crosslinking polyethylene which has a relative viscosity of 2.3 or more and a molecular weight greater than about 3.0 million, as defined by ASTM D-4020-81.

2. An article according to Claim 1 wherein the polyethylene and the crosslinking thereof are such that if the article is subjected to a stress relaxation test in which the article is stretched 3.57 times at 80°C, the recovery force in psi exerted by the article over a period of 0.1 to 30 minutes is at least

$$1750 - 275 \log t$$

where t is the time in minutes.

3. An article according to Claim 2 wherein the recovery force is at least

$$2474 - 275 \log t.$$

4. An article according to Claim 1 which is heat-recoverable.

5. An article according to Claim 1, 2 or 4 wherein the polyethylene has been crosslinked by radiation crosslinking.

6. An article according to Claim 4 which was prepared by a process which comprises expanding an article which is composed of a composition comprising crosslinked polyethylene obtained by crosslinking polyethylene which has a relative viscosity of 2.3 or more and a molecular weight greater than

C

about 3.0 million, as defined by ASTM D-4020-81, said expansion having been carried out at a temperature within the range of room temperature to 140°C.

7. An article according to Claim 6 wherein said expansion was carried out at a temperature within the range of room temperature to 125°C.

8. An article according to Claim 6 prepared by expanding an article which has a substantially circular cross-section having a first diameter to prepare a heat-recoverable article which has a substantially circular cross-section having a second diameter, the second diameter being up to eight times the first diameter.

9. An article according to Claim 6, 7 or 8 wherein the polyethylene has been crosslinked by radiation crosslinking.

10. An article according to Claim 1 obtained by heating a heat-recoverable article to cause recovery thereof, the heat-recoverable article being composed of a composition comprising crosslinked polyethylene obtained by crosslinking polyethylene which has a relative viscosity of 2.3 or more and a molecular weight greater than about 3.0 million, as defined by ASTM D-4020-81.

11. An article according to Claim 10 wherein said heat-recoverable article was prepared by a process which comprises expanding an article which is composed of a composition comprising crosslinked polyethylene obtained by radiation crosslinking polyethylene which has a relative viscosity of 2.3 or more and a molecular weight greater than about 3.0 million, as defined by ASTM D-4020-81, said expansion having been carried out at a temperature within the range of room temperature to 140°C.

12. An article according to Claim 11 wherein said expansion was carried out at a temperature within the range of room temperature to 125°C.

13. An article according to Claim 11 wherein the article was recovered at a temperature within the temperature range of room temperature to 140°C.

14. An article according to Claim 13 wherein the article was recovered at a temperature within the temperature range of 75° to 125°C.

15. An article according to Claim 10, 12 or 14 wherein the polyethylene has been crosslinked by radiation crosslinking.

16. A process for the preparation of a heat-recoverable article, which process comprises

(1) crosslinking an article composed of a composition comprising polyethylene which has a relative viscosity of 2.3 or more and a molecular weight greater than about 3.0 million, as defined by ASTM D-4020-81; and

(2) expanding the crosslinked article from step (1) at a temperature below the melting point of the composition, thus rendering it heat-recoverable.

17. A process according to Claim 16 wherein the polyethylene and the crosslinking thereof are such that if the article is subjected to a stress relaxation test in which the article is stretched 3.57 times at 80°C, the recovery force in psi exerted by the article over a period of 0.1 to 30 minutes is at least

$$1750 - 275 \log t$$

C

where t is the time in minutes.

18. A process according to Claim 17 wherein the recovery force is at least 2474 - 275 log t.

19. A process according to Claim 16 wherein the crosslinked article obtained in step (1) has a first diameter and in step (2) is expanded to a second diameter which is up to eight times the first diameter.

20. A process according to Claim 16 wherein the article is expanded at a temperature within the range of room temperature to 125°C.

21. A process according to Claim 16, 17 or 20 wherein in step (1) the article is crosslinked by radiation.

STRESS RELAXATION AT 120C FOR UNBEAMED SAMPLES

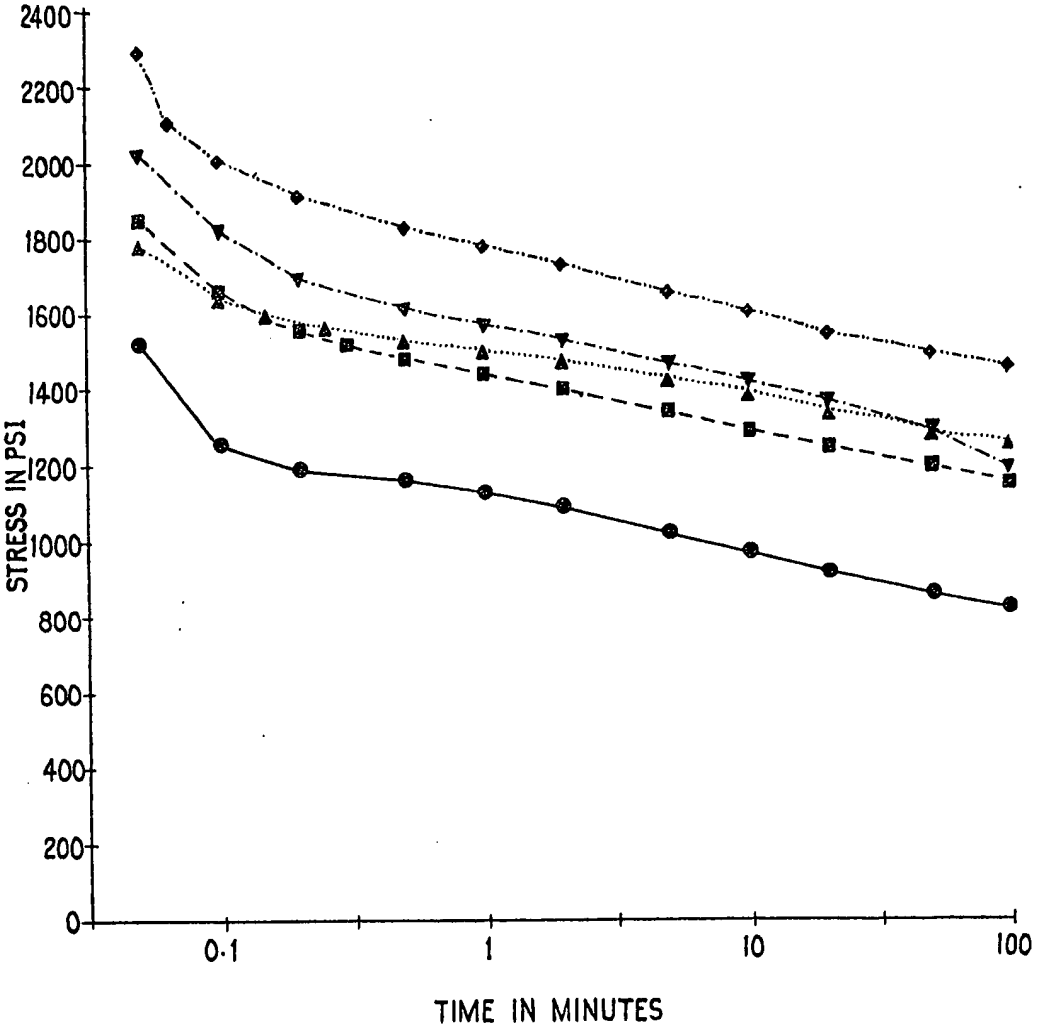


FIG. 1



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STRESS RELAXATION AT 120C FOR BEAMED SAMPLES

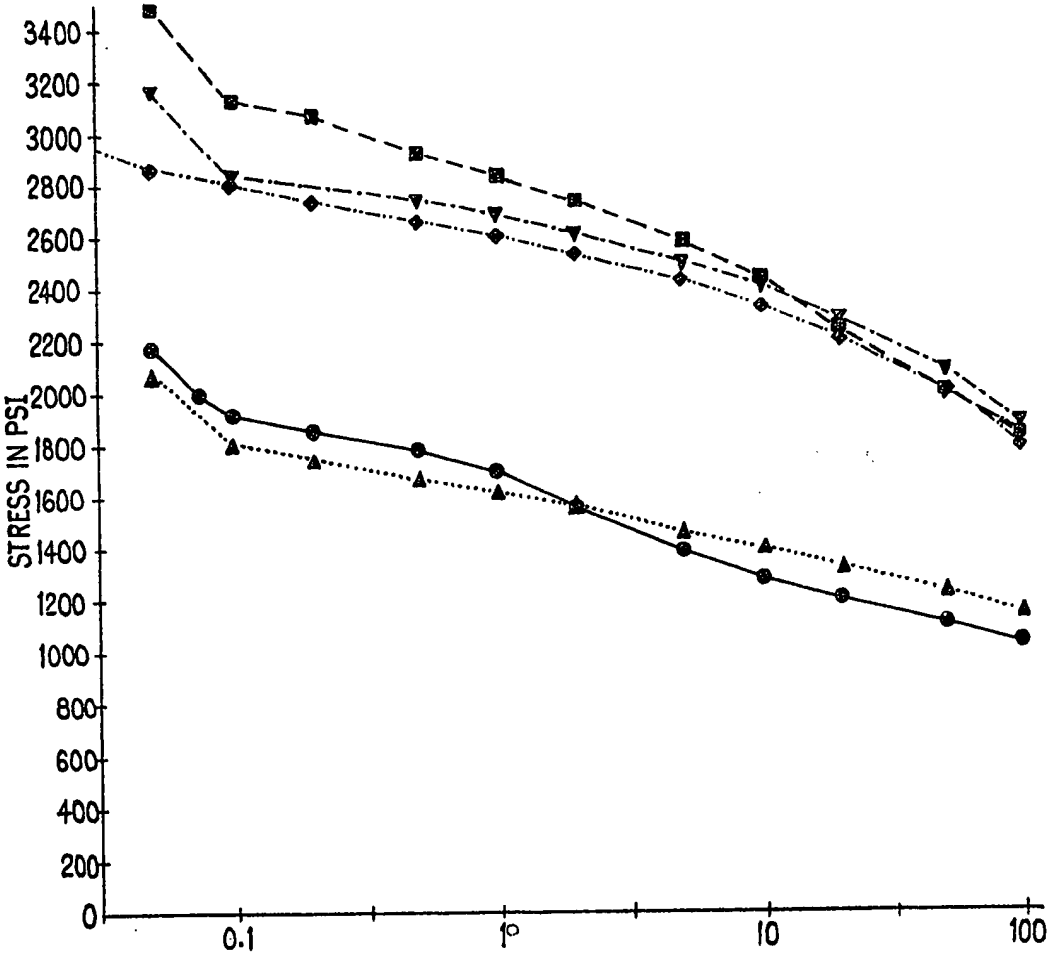


FIG.2

A1

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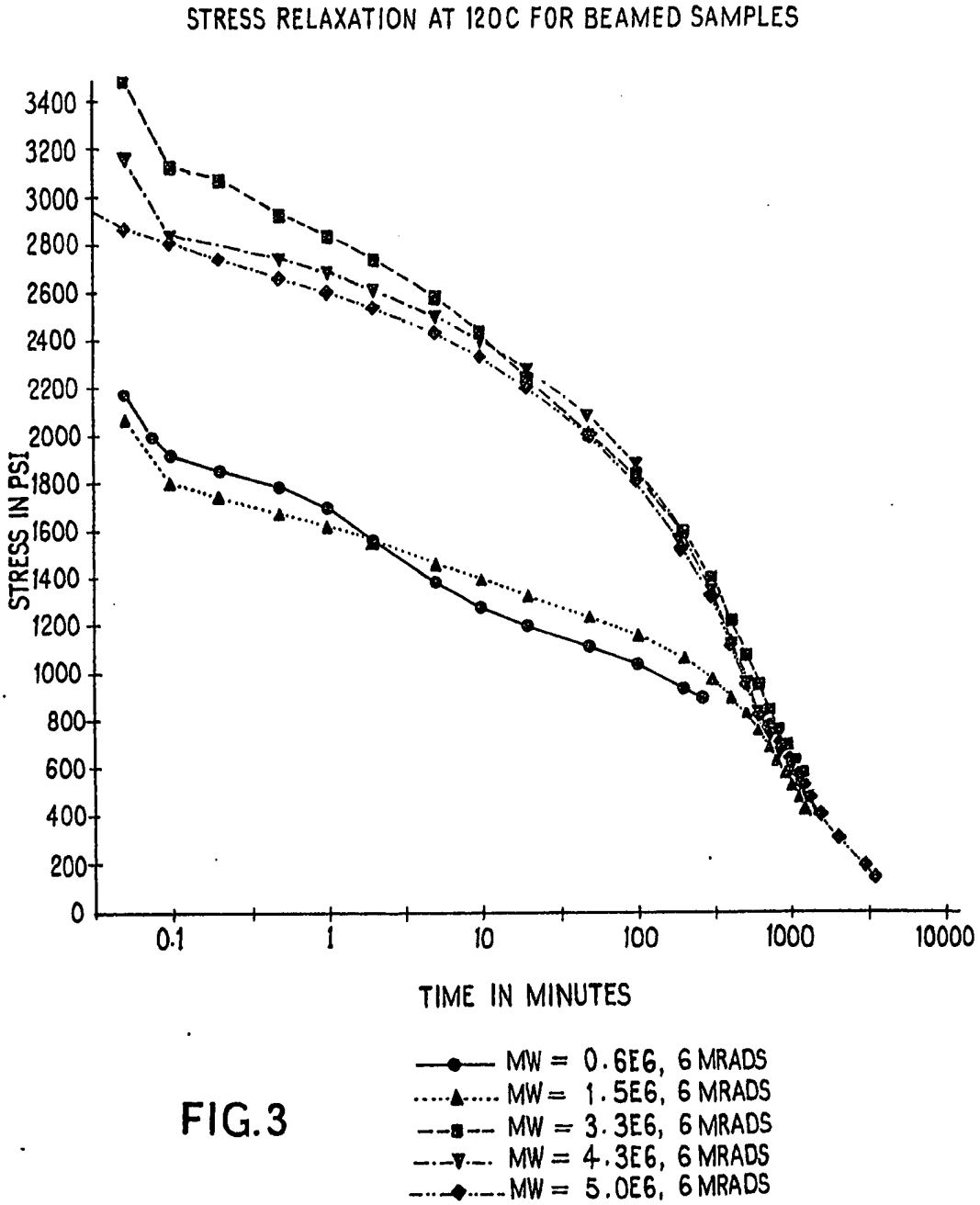


FIG.3

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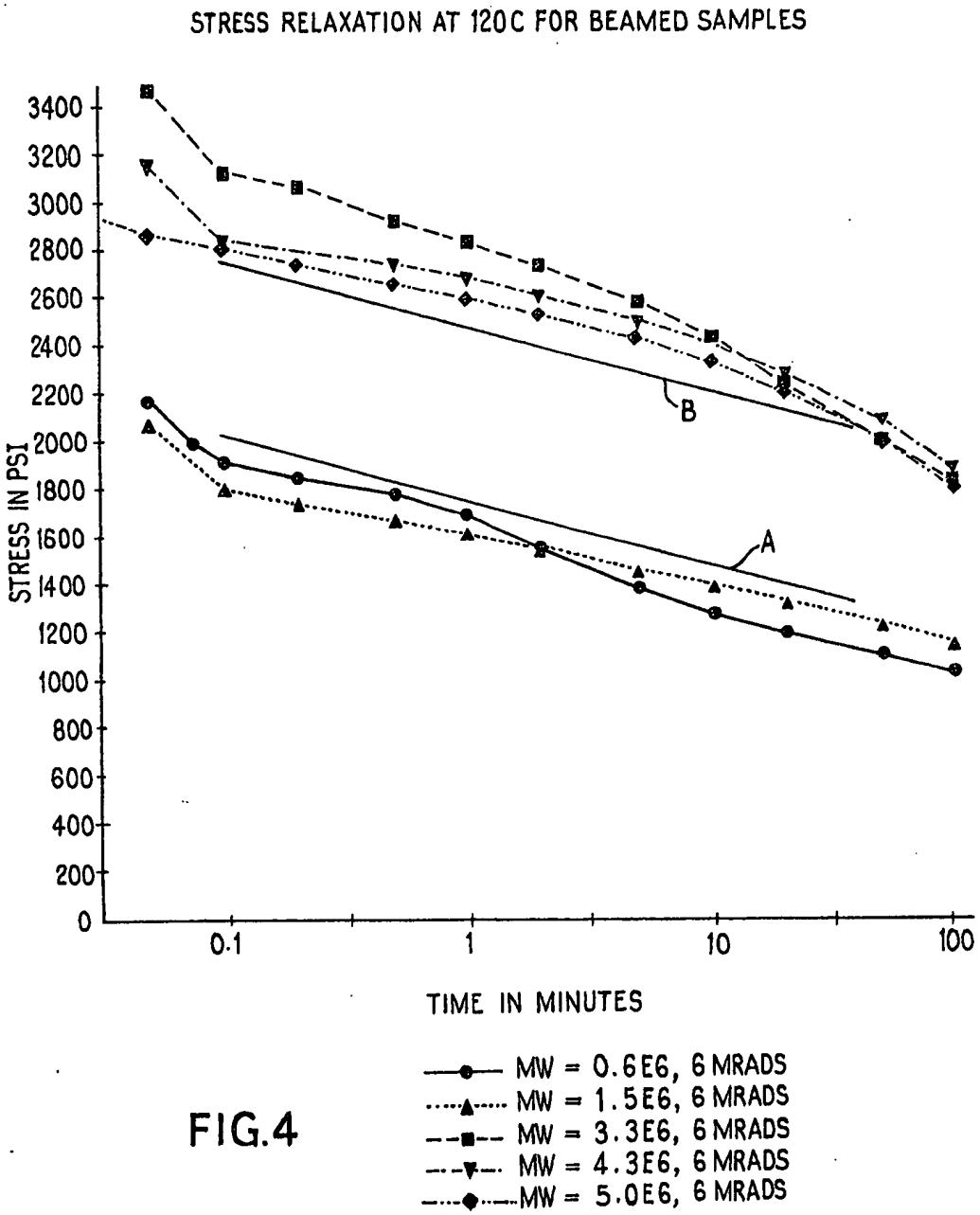


FIG.4

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